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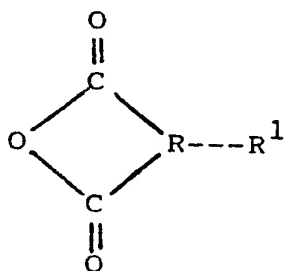
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(64) Method of preparing an improved sizing agent and novel paper sizing method.

(57) Cationically charged water soluble vinyl addition polymers provide improved emulsification of alkenyl succinic anhydride sizing agents. Sized paper products prepared from alkenyl succinic anhydride emulsions made with the polymers have superior ink holdout and strength.

EP 0 151 994 A2

Alkenyl succinic anhydrides (ASA) useful in the sizing of cellulosic materials have gained considerable commercial success. These materials were first fully disclosed in U.S. patent 3,102,064 which is hereinafter incorporated by reference. This patent discloses a certain class of chemical materials generally having the structural formula



wherein R represents a dimethylene or trimethylene radical, and wherein R¹ is a hydrophobic group containing more than 5 carbon atoms which may be selected from the group consisting of alkyl, alkenyl, aralkyl or aralkenyl groups.

In describing the use of the ASA sizes disclosed in this reference, the patentee indicates that for effective utilization, the sizing agents must be used in conjunction with a

material which is either cationic in nature or is, on the other hand, capable of ionizing or disassociating in such a manner to produce one or more cations or other positively charged groups. The cationic agents as they are defined in this reference are disclosed as "alum, aluminum chloride, long chain fatty amines, sodium aluminate, polyacrylamide, chromic sulfate, animal glue, cationic thermosetting resins, and polyamide polymers". The patentee particularly points out as preferred cationic agents various cationic starch derivatives including primary, secondary, tertiary, or quarternary amine starch derivatives and other cationic nitrogen substituted starch derivatives, as well as cationic sulfonium and phosphonium starch derivatives. Such derivatives, as stated by the patentee, may be prepared from all types of starches including corn, tapioca, potato, etc.

With the growing commercial use of sizes of the type above described, serious problems have remained in the application of the sizes to paper stock or pulp prior to its formation into sheet or other useful forms. Part of the problem has been that the ASA sizing materials are not water soluble, and must, accordingly, be uniformly suspended in the pulp so that the size can make adequate contact with the cellulosic fibers and thus create the desired effect on the final product.

While the cationic agents disclosed in U.S. patent 3,103,061 have met with success, there has been a need within the paper

industry to produce a more effective, "cationic agent" for ASA sizes. In addition, such cationic agent would preferably aid in the retention of the size on the fiber, and would increase, where desired, the wet and/or dry strength of the final sheet material.

It is accordingly an object of this invention to provide to the art a group of additives which will serve to emulsify or disperse the ASA size in the pulp and allow for retention of the size onto the fiber.

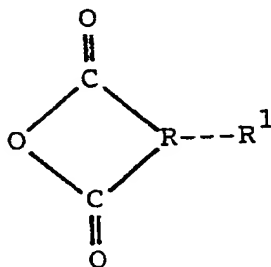
A further object of this invention is the use of water soluble cationic vinyl addition polymers having molecular weights above 10,000 and preferably below 1,000,000 as emulsifiers for ASA sizing materials.

Further objects will appear hereinafter.

The invention, as briefly stated above, is to utilize cationic water soluble vinyl addition polymers having molecular weights greater than 10,000 and preferably below 1,000,000 as additives and emulsifying agents for ASA sizes. The use of such cationic vinyl addition polymers serve as useful emulsifying agents for the ASA size and in addition increases the retention of the size upon the cellulosic sheet.

The ASA sizes to which this invention is applicable include those mentioned in U.S. patents 3,102,061, 4,040,900, 3,968,005, and 3,821,069, all of which are hereinafter incorporated by reference.

The ASA sizes useful in the subject of this invention are generally described by the following structural formula:



wherein R represents a dimethylene or trimethylene radical, and wherein R¹ is a hydrophobic group containing more than 5 carbon atoms which may be selected from the group consisting of alkyl, alkenyl, aralkyl or aralkenyl groups.

In a particular useful embodiment of this invention, a surfactant has also been employed in making the ASA sizes of this invention. This surfactant may be anionic, non-ionic, or cationic in nature. Surfactants employed are generally water soluble and have HLB values ranging from about 8 to about 30 or higher, and preferably from about 8-15. The surfactant is generally used to prepare the ASA size by simply mixing it with the raw ASA material. The ASA size used in this invent-

ion accordingly, and in a preferred embodiment of this invention, will generally contain 75-99.5 parts by weight of ASA and preferably 90-99 parts by weight of ASA with 0.5-25 parts, preferably .75-10 parts, and most preferably 1.0-5 parts by weight of surfactant.

The surfactants are preferably added to the ASA prior to emulsification in the aqueous medium. The surfactants can also be added to the aqueous medium prior to the addition of the ASA.

The surfactants useful in this invention are further described in U.S. patent 4,040,900 previously incorporated by reference into this specification. The relevant parts of U.S. patent 4,040,900 begin at column 4, line 54 continue through column 5, line 46. Other portions of this patent are, however, relevant.

Classes of materials useful as the surfactants in this invention include: ethoxylated alkyl phenols, such as nonyl phenoxy polyethoxy ethanols and octyl phenoxy polyethoxy ethanols; poly ethyleneglycols such as PEG 400 mono-oleate, and PEG 600 dilaurate; as well as other materials including certain ethoxylated phosphate esters.

Preferred surfactants for use in our invention are GAFAC RM510 and GAFAC RE610, both free acids of complex organic

phosphate esters, manufactured by the GAF Corporation.

THE WATER SOLUBLE POLYMERS

Water soluble polymers which are useful cationic agents in this invention include water soluble vinyl addition homopolymers and copolymers having molecular weights greater than 10,000 and preferably below 1,000,000 where at least 10 weight percent and up to 100 weight percent of the mer content of the polymer is a cationic monomer, or cationically modified monomer. Preferably at least 15 and up to 95 weight percent of the mer units in the polymer may be cationic or cationically modified monomers. Most preferably from 20-75 percent by weight of the mer units in the polymer or copolymer are cationic or cationically modified.

The polymers selected for use in this invention generally have a molecular weight of greater than 10,000 and preferably less than 1,000,000. Polymers of this type should generally be water soluble, and a preferred molecular weight has been found to be between 20,000 and 750,000. Most preferably, the molecular weights of the polymers employed range from 50,000 to 150,000.

Polymers which can be employed in the practice of this invention include, but are not limited to the following exemplary copolymers and homopolymers: acrylamide-dimethyl-

aminoethylacrylate, acrylamide-dimethylaminoethylacrylate quaternaries, acrylamide-diethylaminoethylacrylate, acrylamide-diethylaminoethylacrylate quaternaries, acrylamide-dimethylaminoethylmethacrylate, acrylamide-dimethylaminoethylmethacrylate quaternaries, acrylamide-diallyldimethyl ammonium chloride, polydiallyl-dimethyl ammonium chloride, polydimethylaminoethylmethacrylate and its quaternaries, polymethacrylamidopropyltrimethyl ammonium chloride; and, acrylamide-methacrylamidopropyltrimethyl ammonium chloride.

Also useful are polymers and copolymers of acrylamide which have been subjected to a "Mannich" reaction with formaldehyde and a lower alkyl secondary amine. These polymers may or may not be quaternized.

Also useful in the practice of this invention are certain condensation polymers such as those prepared by condensing dimethylamine with epi-chlorohydrin. Polymers of this type are described in Reissue Patents 28,807 and 28,808, hereafter incorporated by reference. Polymers of this type typically have intrinsic viscosities in the range of 0.15 to 1.5. Other cationic water soluble condensation polymers such as those prepared from ethylene dichloride and ammonia, which may or may not be quaternized with methylchloride, etc. may also be useful. While the bulk of this specification refers

to polymers of this invention as vinyl addition polymers, the description is also applicable to those condensation polymers.

As seen, all of the polymers useful in this invention are cationically charged and are water-soluble. Many are prepared from vinyl addition monomers, although condensation polymers will also work. Since the number of possible cationically charged monomers that will produce a water soluble polymer is essentially unlimited, and it is expected that all water-soluble cationically charged vinyl addition polymers having a molecular weight of 10,000 or more but less than 1,000,000 will work, we do not wish to be limited to the above given list. However, the mentioned compounds are preferred ones.

The polymers employed, as stated above, may be copolymers and even terpolymers of various vinyl addition monomers. While acrylamide is a preferred nonionic monomer for use in preparing copolymers useful in this invention, other nonionic monomers such as methacrylamide and even certain anionically charged monomers such as acrylic acid, methacrylic acid, various sulfonated water soluble vinyl addition monomers, etc. can be employed.

Polymers as used in this invention may be in the form of water-in-oil emulsions (such as those described in U.S. Re. patent 28,474 and 28,576, both of which are hereinafter in-

corporated by reference), dry powders, or dilute aqueous solutions. Preferably the polymers form an oil-in-water emulsion of the alkenyl succinic anhydride sizing material.

In order to employ the polymers of the subject invention in the emulsification of ASA sizes, an aqueous solution must first be prepared of the polymer. In the case of the water-in-oil emulsions of vinyl addition polymers, we have found the water soluble surfactants used to invert the water-in-oil emulsions have no detrimental effect on the activity of the polymer used to emulsify the ASA size. When preparing a polymer solution from a water-in-oil emulsion polymer, a useful method or device for forming the solution is exemplified in U.S. Patent 4,057,223 which discloses a mixing block.

Depending upon the molecular weight and cationic charge of the polymer, from 0.01 % to 25 %, and preferably .01-10 % by weight of the final size emulsion to be added to the pulp furnish may be polymer.

The ASA emulsions fed to the pulp slurry according to this invention will generally contain:

50 - 99.9 % by weight water
.01 - 50 % by weight ASA
.001 - 25.0 % by weight (preferably .005 - 3.0 %)
of the water soluble polymer

Preferably, these emulsions will contain:

60 - 99.9 % water
.01 - 40 % ASA
.010 - 10 % polymer

Most preferably the ASA emulsion contains .01 - 5.0 and generally .01 - 1.0 parts polymer and even more preferable, .05 - .9 parts polymer for each part of ASA in the emulsion.

Most preferably the ASA emulsion contains .01 - 7.5 and generally .01 - 5.0 parts polymer.

The polymers are thus used in preparation of the dispersions or emulsions of the ASA sizing material.

The polymers of this invention may be used to emulsify the ASA, or may be added to previously formed ASA emulsions. In either case, the polymer will increase the performance of the emulsion compared to emulsions not containing the polymer. When the polymer is added to an ASA emulsion that has already been formed, conventional emulsifying agents should be used in addition to the polymer. When added or used during the make-up of the ASA emulsion, no additional emulsifier need be employed.

In order to test the subject invention, the following ex-

periments were conducted. The polymers listed below were obtained commercially or prepared in the form indicated.

EXAMPLE 1

Solution acrylamide copolymers of types DMAEM-MeCl Quat, MAPTAC, and polyDADMAC of molecular weights ranging from 10,000 to 400,000 were evaluated as ASA emulsification and retention aids. These novel sizing compositions were compared in terms of ASA particle size, physical emulsion stability and sizing performance to conventional ASA emulsions in water or cationic starch. Description of these polymers are given in Table I.

ASA emulsions in water were prepared by combining 95 parts of distilled water and 5 parts of ASA in an Eberbach semi-micro-emulsion cup. The mixture was dispersed for 3 minutes at high speed. The emulsion formed was diluted with distilled water to 0.50 percent ASA solids basis and used in Example 1. ASA emulsions in cationic starch were prepared by first hydrating 5 parts of a pregelatinized cationic potato starch in 95 parts of water and agitating for 30 minutes. Size emulsions were then prepared by combining 75 parts of the starch solution with 25 parts of ASA in the emulsion cup and dispersing for 20 seconds. This emulsion was diluted to 0.50 percent ASA solids basis and used in Example 2. Lastly, ASA emulsions in vinyl addition polymers were prepared by dispersing ASA in

polymer solutions at a ratio of 5:1 dry solids basis. These emulsions were diluted to 0.50 percent ASA solids basis by the method described above. Examples 3-8 illustrate the novel use of these addition polymers.

The examples 26 and 27 illustrate the use of dimethylamino epi-chlorohydrin condensation polymers having an intrinsic viscosity of at least 0.15.

The ASA emulsions were tested separately in a paper slurry of composition 50 percent recycled corrugated boxboard, 50 percent recycled newsprint. Other slurry parameters were 0.5 percent consistency, 400 Canadian Standard Freeness, pH 7.5, and 25 degrees Celsius to which was added 12.5 parts per million of hydrated aluminum sulfate. Handsheets of basis weight 50 pounds per 3300 square feet were prepared in accordance with TAPPI T-205 procedures. The sizing compositions listed above were added to the paper slurry shortly before wet-web formation at dosages of 0.10 and 0.15 percent on paper solids. Handsheets were immediately dried on rotary drum to 98 percent solids basis. Results are shown on Table I.

TABLE I

Designation	Polymer Description	Weight Ratio	Molecular Weight ¹ calculated from (Intrinsic Viscosity)
A	diallyldimethyl ammonium chloride Quat.	-	82,000 (0,55)
B	diallyldimethyl ammonium chloride Quat.	-	235,000 (1,08)
C	acrylamide - DMAEM methylchloride Quat.	75:25	40,000 (0,44)
D	acrylamide - DMAEM methylchloride Quat.	75:25	210,000 (1,27)
E	acrylamide - MAPTAC	75:25	50,000 (0,40)
F	acrylamide - MAPTAC	75:25	380,000 (1,47)
N	dimethylamine epi-chlorohydrin	-	- (0,24)
O	dimethylamine epi-chlorohydrin	-	- (0,25)

Example No.	Medium for Size ² Emulsifications	Ratio of Average Size to Medium Solids	Particle Size of Emulsion (Microns)	Physical Emulsion ⁴ Stability (Form)	Acid Ink Penetration Test (in seconds) ⁵ Versus Percent by Weight of Size on Pulp Solids 0.100% 0.150%
1	Distilled Water	-	2-10	Nonstable, two distinct phases	2 15
2	Cationic Potato Starch(STALOK 500) ³	5:1	1-2	Nonstable, precipitated settled	157 377
3	Polymer A	5:1	0.5-2	Nonstable, two distinct phases	191 392
4	Polymer B	5:1	1-2	Stable	263 434
5	Polymer C	5:1	1-3	Stable	116 249
6	Polymer D	5:1	0.5-2	Stable	157 322
7	Polymer E	5:1	1-2	Stable	71 204
8	Polymer F	5:1	1-2	Stable	135 278
26	Polymer N	5:1	0.5-2	Stable	- 151
27	Polymer O	5:1	1-3	Stable	- 211

TABLE I

- 1 Intrinsic Viscosity $(\eta)_I$ run in 1M NaNO_3 at 30°C
Molecular weights (MW) calculated from Mark-Houwink Equation: $(\eta)_I = (K) (\text{MW})^2$
- 2 Commercial paper grade alkenyl succinic anhydride
- 3 Available from A. E. Staley, Decatur, Illinois
- 4 Physical emulsion form after one week, room temperature aging
- 5 Hercules' size test apparatus conducted at 80% reflectance with
1% formic acid, 1.25% naphthol green test ink

EXAMPLE 2

Vinyl addition polymers, such as copolymers of acrylamide with DMAEM-MeCl quat or MAPTAC, and polyDADMAC, were further evaluated as ASA emulsification and retention aids. These novel sizing compositions were compared in terms of ASA emulsion particle size, physical emulsion stability with aging, and sizing performance to conventional ASA emulsions in water or cationic starch. The molecular weight of these polymers ranged from 10,000 to 400,000. A description of these polymers is shown in Table II.

ASA emulsions in water were prepared by combining 95 parts of distilled water and 5 parts of ASA in a laboratory 8 ounce Osterizer cup. The mixture was dispersed at high speed for 3 minutes. The emulsion formed was diluted with distilled water to 0.50 percent ASA solids basis and used in Example 9. ASA emulsions in cationic starch solutions were prepared by first hydrating 5 parts of a pregelatinized cationic potato starch in 95 parts of water and agitating for 30 minutes. Size emulsions were then prepared by combining 95 parts of the starch solution with 5 parts of ASA in the Osterizer cup and dispersing the size for 25 seconds. This emulsion was diluted to 0.50 percent ASA solids basis and used in Example 10. ASA emulsions in vinyl addition polymers were prepared by dispersing ASA in the polymer solutions at a ratio of 1:1 ASA to polymer solids in the Osterizer cup for 5 to 30 seconds.

These emulsions are then diluted to 0.50 percent ASA solids as described above. Examples 11-16 illustrate the novel use of these vinyl addition polymers.

Each ASA emulsion was tested separately in a paper slurry of composition 50 percent bleached softwood kraft and 50 percent bleached hardwood kraft pulps. The other slurry parameters were 0.5 percent consistency, 330 Canadian Standard Freeness, pH 7.3, and 27 degrees Celcius. Handsheets of basis weight 50 pounds per 3300 square feet were prepared in accordance with TAPPI T-205 procedures. The sizing compositions listed below were added to the paper slurry shortly before wet web formation at the dosage of 0.20 percent ASA solids on paper solids. Handsheets were immediately pressed to approximately 50 percent residual moisture and dried on a rotary drum dryer to 98 percent paper solids basis. Results are shown in the attached Table II.

TABLE II

Designation	Polymer Description	Weight Ratio Acrylamide to Quat	Molecular Weight ¹ calculated from (Intrinsic Viscosity)
A	diallyldimethyl ammonium chloride Quat.	-	82,000
B	diallyldimethyl ammonium chloride Quat.	-	235,000
F	acrylamide - MAPTAC	75:25	380,000
G	acrylamide - MAPTAC	50:50	140,000
D	acrylamide - DMAEM methyl chloride Quat.	75:25	210,000
H	acrylamide - DMAEM methyl chloride Quat.	50:50	90,000

Example No.	Medium for ASA ² Emulsification	Ratio of ASA to Medium Solids	Average Particle Size of ASA (Microns)	Physical ⁴ Emulsion Stability (Form)	Neutral Ink Penetration Test ⁵ (Seconds) at 0.40% ASA on Pulp Solids
9	Distilled Water	-	1-5	Nonstable, two distinct phases	< 1
10	Cationic Potato Starch(STALOK 500) ³	1:1	1-3	Nonstable, precipitate settled	273
11	Polymer A	1:1	1-3	Nonstable, two distinct phases	9
12	Polymer B	1:1	1-3	Stable	5
13	Polymer F	1:1	0.5-2	Stable	71
14	Polymer G	1:1	1-2	Stable	246
15	Polymer D	1:1	0.5-1	Stable	227
16	Polymer H	1:1	0.5-2	Stable	17

- Intrinsic Viscosities (n)_I run in 1M NaNO₃ at 30°C
 - Molecular weights (MW) calculated from Mark-Houwink Equation: (n)_I=(K) (MW)²
 - Commercial paper grade alkenyl succinic anhydride
 - Available from A. E. Staley, Decatur, Illinois
 - Physical emulsion form after one week, room temperature aging
- Hercules' size test apparatus conducted at 80% reflectance with 1 % sodium formate (pH 7.0) and 1.25 % naphthol green test ink

EXAMPLE 3

The following examples further illustrate the novel use of acrylamide copolymers of type DMAEM-MeSQ, DMAEA-MeSQ, DEAEA-MeSQ and DADMAC of molecular weights greater than 1,000,000 as emulsifiers and retention aids for alkenyl succinic anhydride sizing compositions. The ASA emulsions thus formed were compared in the terms of particle size and sizing performance with respect to ASA water emulsions and conventional emulsions prepared from cationic starch.

For comparison, ASA emulsions in water were prepared by combining 95 parts of distilled water and 5 part of ASA in an Eberbach semi-microemulsion cup and dispersing the size for 60 seconds. The resulting emulsion was diluted to 0.50 percent ASA solids basis with water and used in Example 17. The ASA emulsions in cationic starch were prepared by first hydrating three parts of a pregelatinized cationic potato starch in 97 parts agitated cold water for 30 minutes. Emulsions were then prepared at two ASA to starch solid ratios of 10:1 and 3:1 by dispersing 30 parts of ASA in 70 parts of 3 percent cationic starch or 9 parts of ASA in 91 parts of 3 percent cationic starch respectively with the aid of the semi-microemulsion cup. The resulting emulsions were diluted to 0.5 percent ASA solids basis with water and used in Examples 19 and 20 accordingly.

Polymer solutions were prepared by hydrating 0.6 parts (as polymer solids) of those copolymers of acrylamide listed below in 99.4 parts of water respectively, allowing sufficient time and mixing for complete hydration. Emulsions were then prepared at two ASA to polymer solids ratios of 10:1 and 3:1 by dispersing 6 parts of ASA in 94 parts of 0.6 percent polymer solids solution or 1.8 parts of ASA in 98.2 parts of 0.6 percent polymer solids solution respectively with the aid of the semi-microemulsion cup.

A further dilution to 0.5 percent ASA solids was then taken. The following examples illustrate the advantages offered by this invention: the ability of these cationic water soluble acrylamide copolymers to initiate an ASA emulsion and to render the ASA emulsion particles cellulose substantive.

Each of the below cited ASA emulsions were separately added to a 0.5 percent consistency pulp slurry of composition 40 percent bleached hardwood sulfate pulp, 40 percent bleached softwood sulfate pulp, and 20 percent calcium carbonate of 300 Canadian Standard Freeness (pH 8.2). Handsheets of basis weight 50 pounds per 3300 square feet were prepared in accordance with TAPPI T-205 procedures. Emulsions of ASA were added to the pulp slurry shortly before wet-web formation at dosages of 0.250 and 2.00 percent on dry pulp solids. Handsheets were immediately dried on a rotary drum dryer to 98 percent solids basis (2 percent residual moisture). Results

are shown in Table III.

This example clearly illustrates the novel use of cationic vinyl addition copolymers as ASA emulsification aids and retention aids. Improved water resistance is realized over conventional ASA in water or cationic starch emulsions. Secondly, the improved water resistance offered by this invention cannot be attributed simply to improved papermachine retention as demonstrated by separate additions of these same cationic polymers to the paper furnish.

The use of polymers in the high molecular weight range, however, can lead to the formation of tacky deposits and unstable emulsions. Further research as exemplified herein has shown that polymers having a molecular weight greater than 10,000 but lower than 1,000,000, and preferably from 20,000 to 750,000, performed essentially equivalent to polymers having higher molecular weight. In addition, the use of polymers having molecular weights in the preferred range of from 50,000 - 150,000 led to the elimination of the deposit formation noted above, and increased the stability of the ASA emulsions so prepared.

TABLE III

Designation		Acrylamide Copolymer Quats		Molecular Weight ¹ calculated from Intrinsic Viscosity		Form	
I		DMAEA, methylchloride quat.					
J		12 wt. %-DEAEA, monomethyl sulfate quat.		5,700,000		dry powder	
K		12.5 wt. %-DMAEM, dimethyl sulfate quat.		9,200,000		dry powder	
L		35 wt. %-DMAEM, monomethyl sulfate quat.		-		dry powder	
M		28.6 wt. %-DADMAC		8,900,000		emulsion	
				4,300,000		emulsion	

Example No.	Medium for Size ² Emulsification	Ratio of Size To Medium Solids	Avg. Particle Size of Emulsion (microns)	Neutral Ink Penetration Test ⁵ (in seconds) vs. Percent By Weight Size on Dry Pulp Solids	
				0.250%	2.000%
17	Distilled Water	-	2-20	1	423
18	Distilled Water Plus Surfactant ³	-	1-4	1	255
19	Cationic Potato Starch (STALOK 400) ⁴	3:1	1-2	310	-
20	STALOK 400 ⁴	10:1	1-3	282	-
21	Polymer I	3:1	1-3	656	-
22	Polymer J	3:1	1-3	426	-
23	Polymer K	3:1	1-3	464	-
24	Polymer L	10:1	0.5-4	468	-
25	Polymer M	10:1	0.5-2	313	-

1 Intrinsic Viscosity (n)_I run in 1M NaNO₃ at 30°C. Molecular weights (MW) calculated from Mark Houwink Equation: (n)_I=(K) (MW)².

2 Commercial paper grade ASA

3 Surfactant type: nonylphenol ethoxylate dosed at 5.0 % by weight of sizing agent

4 Available from A. E. Staley, Decatur, Illinois

5 Hercules' size test apparatus conducted at 80 % reflectance

DMAEA = dimethylaminoethylacrylate

DEAEA = diethylaminoethylacrylate

DMAEM = dimethylaminoethylmethacrylate

DADMAC = diallyldimethylammoniumchloride

EXAMPLE 4

The effect of various other polymers on the emulsification of ASA sizing materials and the results obtained using such polymers were investigated. In this group of experiments, 3 different classes of polymers were employed (see below). All of these materials were prepared as water-in-oil emulsions of the polymer. Aqueous solutions of the polymers were prepared to yield an approximate 2% product basis or approximately .6% by weight aqueous polymer solution. The polymer solution was prepared by mixing together 288 grams of deionized water, 6.0 mls. of a 2% by weight aqueous solution of an ethoxylated (9) nonyl phenol surfactant followed by adding approximately 6 cc of the water-in-oil emulsion to the stirred mixture. The aqueous solutions were then adjusted to yield 2% by weight polymer product.

The ASA chosen for this and all subsequent studies is a substituted (alkenyl) cyclic dicarboxylic acid anhydride wherein the alkenyl groups are derived from a mixture of 14-22 carbon atoms.

The ASA size measure used in these tests was prepared by mixing 196 gms. of the polymer solution with 4.0 gms. of a commercial paper grade alkenyl succinic anhydride size available from Chevron Chemical Company, containing 1.0% by weight of Gafac RM-510 surfactant available from GAF Corporation. The

resultant mixture was then emulsified by mixing for 30 seconds in an Eberbach semi-microemulsion cup followed by a final dilution of 0.5% ASA solids. The ASA emulsions were added to a commercial, calcium carbonate filled bleached Kraft furnish dosed at 0.25 % on dry pulp solids.

The neutral ink penetration test describes the paper's resistance to aqueous fluid penetration and is a measurement of time (in seconds) for ink to penetrate paper to a predetermined degree (80 percent reflectance endpoint). The greater the time, the greater the paper's resistance to ink penetration. Those skilled in the art will readily recognize this test as the generally practiced Hercules' Size Penetration Test. Results are found in Table IV.

<u>Polymer</u>		<u>Mole Ratio</u>
P	Acrylamide-MAPTAC	97.5:2.5
Q	" "	95 :5
R	" "	85 :15
S	Acrylamide-DMAEA-Q	97.5:2.5
T	" "	95 :5
U	" "	85 :15
V	Acrylamide-DMAEM-Q	97.5:2.5
W	" "	95 :5
X	" "	85 :15
Y	" "	92.3:7.7

TABLE IV

Example No.	Medium For Size ¹ Emulsifications	Ratio of Size to Medium Solids	Average Particle Size of Emulsion (Microns)	Acid Ink ² Penetration Test (in seconds)
28	Distilled Water	-	3 - 15	4
29	Cationic Corn Starch (CATO F) ³	1 : 2.5	2 - 3	605
30	Polymer P	1 : 0.3	2 - 5	-
31	Polymer Q	1 : 0.3	1 - 3	427
32	Polymer R	1 : 0.3	1 - 3	464
33	Polymer S	1 : 0.3	1 - 3	711
34	Polymer T	1 : 0.3	1 - 3	642
35	Polymer U	1 : 0.3	1 - 3	1069
36	Polymer V	1 : 0.3	0.5 - 2	284
37	Polymer W	1 : 0.3	0.5 - 2	629
38	Polymer X	1 : 0.3	1 - 3	815
39	Polymer Y	1 : 0.3	1 - 3	528

- 1 Commercial paper grade alkenyl succinic anhydride
- 2 Hercules' size test apparatus conducted at 80% reflectance using pH 2 acid ink from Monsanto, St. Louis, Missouri
- 3 Available from National Starch Company, Bridgewater, New Jersey

EXAMPLE 5

The following examples further illustrate the novel use of acrylamide copolymers of type DMAEM-MeSQ and DADMAC as emulsifiers and retention aids for alkenyl succinic anhydride sizing compositions. The ASA emulsions thus formed were compared in terms of particle size and sizing performance with respect to ASA water emulsions and conventional emulsions prepared from cationic starch.

For comparison, ASA emulsions in water were prepared by combining 95 parts of distilled water and 5 parts of ASA in an Eberbach semi-microemulsion cup and dispersing the size for 60 seconds. The resulting emulsion was diluted to 0.50 percent ASA solids basis with water and used for the two sets. The ASA emulsions in cationic starch were prepared by first hydrating three parts of a pregelatinized cationic potato starch in 97 parts agitated cold water for 30 minutes. Emulsions were then prepared at two ASA to starch solid ratios of 10:1 and 1:1 by dispersing 30 parts of ASA in 70 parts of 3 percent cationic starch or 3 parts of ASA in 97 parts of 3 percent cationic starch respectively with the aid of the semi-microemulsion cup. The resulting emulsions were diluted to 0.5 percent ASA solids basis with water and used accordingly.

Polymer solutions were prepared by hydrating 0.6 parts (as

polymer) of those copolymers of acrylamide listed below in 99.4 parts of water respectively, allowing sufficient time and mixing for complete hydration. Emulsions of ASA in polymer were then prepared by dispersing 6 parts of ASA in 94 parts of 0.6 percent polymer for 60 seconds with the aid of the semi-microemulsion cup. A further dilution to 0.5 percent ASA solids was then taken. Also this example illustrates the advantages offered by this invention: the ability of these cationic water soluble acrylamide copolymers to initiate and maintain a stable ASA emulsion and to render the ASA emulsion particles cellulose substantive. Polymers tested include the following:

<u>Polymer</u>	<u>Mole Percent (M%)</u>
	<u>Acrylamide Copolymer Quat</u>
AA	3.5 M% DMAEM ¹ -MeSQ
BB	7.7 M% DMAEM-MeSQ
CC	10.9 M% DMAEM-MeSQ
DD	3.2 M% DADMAC ²
EE	5.0 M% DADMAC
FF	15.0 M% DADMAC

¹ Dimethylaminoethylmethacrylate methylsulfate quat.

² Diallyldimethylammonium chloride

Each of the below cited ASA emulsions were separately added to a 0.5 percent consistency pulp slurry of composition 40

percent bleached hardwood sulfate pulp, 40 percent bleached softwood sulfate pulp, and 20 percent calcium carbonate of 300 Canadian Standard Freeness (pH 8.2). Handsheets of basis weight 50 pounds per 3300 square feet were prepared in accordance with TAPPI T-205 procedures. Emulsions of ASA were added to the pulp slurry shortly before wet-web formation at dosages ranging from 0.125 to 2.00 percent. Handsheets were immediately dried on a rotary drum dryer to 98 percent solids basis (2 percent residual moisture). In another variation of this procedure, 0.025 percent of a polymer was added to the pulp slurry separately after addition of sizing emulsions. Results are shown in Table V.

This example clearly illustrates the novel use of cationic vinyl addition copolymers as ASA emulsification aids and emulsion retention aids. Improved water resistance is realized over conventional ASA in water or cationic starch emulsions. Secondly, the improved water resistance offered by this invention cannot be attributed simply to improved paper-machine retention as demonstrated by separate additions of these same cationic polymers to the paper furnish.

TABLE V

Example No.	Medium ¹ for Size Emulsifications	Ratio of Size of Medium Solids	Average Particle Size of Emulsion (Microns)	Separate polymer ² Addition Percent	Neutral Ink Penetration Test (seconds) ³ Percent by Weight Size on Pulp Solids			
					0.125	0.250	1.000	
40	Distilled Water	-	2-10	None	-	1	11	
41	Distilled Water	-	2-10	0.025	-	3	535	
42	Cationic Potato Starch (STALOK 400) ⁴	10:1	1-3	None	23	282	-	
43	Polymer AA	10:1	1-4	None	20	451	-	
44	Polymer BB	10:1	1-4	None	32	471	-	
45	Polymer BB	10:1	1-4	0.025	24	510	-	
46	Polymer CC	10:1	0.5-4	None	16	468	-	
47	Polymer DD	10:1	0.5-2	None	4	226	-	
48	Polymer EE	10:1	0.5-2	None	-	260	-	
49	Polymer FF	10:1	0.5-2	None	-	313	-	
50	Polymer FF	10:1	0.5-2	0.025	28	445	-	

- 1 Commercial paper grade alkenyl succinic anhydride
- 2 A 7.7 mole percent DMAEM-methyl sulfate copolymer with acrylamide
- 3 Hercules' size test apparatus conducted at 80% reflectance using neutralized 1% formic acid test ink to pH 7.0
- 4 Available from A. E. Staley Company, Decatur, Illinois

Claims

1. In an improved method for the preparation of an emulsified alkenyl succinic anhydride sizing agent useful in the preparation of sized paper products, such emulsion containing water, an alkenyl succinic anhydride, and a cationic agent, the improvement comprising using as the cationic agent a water soluble cationic vinyl addition polymer having a molecular weight of at least 10,000 and preferably of between 10,000 and 1,000,000.

2. The method of claim 1 wherein the cationic vinyl addition polymer is selected from water soluble vinyl addition polymers having molecular weights greater than 10,000 and preferably less than 1,000,000, said polymer having at least 10 weight percent and up to 100 weight percent of the mer content of the polymer made from a cationic or cationically modified vinyl addition monomer.

3. The method according to one of claims 1 or 2 wherein the cationic or cationically modified vinyl addition monomer is selected from the group consisting of:

a) diallyldimethyl ammonium chloride;

- b) methacrylamidopropyltrimethyl ammonium chloride;
- c) dimethylaminoethylmethacrylate;
- d) dimethylaminoethylmethacrylate quaternaries;
- e) dimethylaminoethylacrylate;
- f) dimethylaminoethylacrylate quaternaries;
- g) diethylaminoethylacrylate;
- h) diethylaminoethylacrylate quaternaries;
- i) acrylamide reacted with formaldehyde and a lower secondary amine through the Mannich reaction; and
- j) manniched acrylamide quaternaries.

4. The method according to one of claims 1 to 3, wherein the polymer is present in the alkenyl succinic anhydride size emulsion at a level of from 0.01 - 10.0 percent by weight polymer solids.

5. The method according to one of claims 1 to 4 wherein the polymer is present in the alkenyl succinic anhydride size emulsion at a level of from 0.01 - 5.0 percent by weight polymer solids.

6. The method according to one of claims 1 to 5 wherein the polymer is added to the alkenyl succinic anhydride size emulsion so as to provide from .05 - .9 part by weight polymer for each part of alkenyl succinic anhydride present in such emulsion.

7. In a method for the sizing of paper using an alkenyl succinic anhydride size wherein an emulsion of alkenyl succinic anhydride is applied to the paper stock, the improvement comprising using as an emulsifier for the alkenyl succinic anhydride size, a water soluble cationic vinyl addition polymer having a molecular weight greater than 10,000 and preferably less than 1,000,000.

8. The method of claim 7 wherein the cationic water soluble vinyl addition polymer is selected from the group consisting of homo and copolymers of one or more of the following monomers:

- a) diallyldimethyl ammonium chloride;
- b) methacrylamidopropyltrimethyl ammonium chloride;
- c) dimethylaminoethylmethacrylate;
- d) dimethylaminoethylmethacrylate quaternaries;
- e) dimethylaminoethylacrylate;
- f) dimethylaminoethylacrylate quaternaries;
- g) diethylaminoethylacrylate;
- h) diethylaminoethylacrylate quaternaries;
- i) acrylamide reacted with formaldehyde and a lower secondary amine through the Mannich reaction; and
- j) manniched acrylamide quaternaries.

9. The method of claims 7 or 8 wherein the emulsion containing the water soluble polymer is added to the paper

stock.

10. An emulsion of alkenyl succinic anhydride comprising:

- a) 50 - 99.9 percent by weight water
- b) .01 - 40 percent by weight of an alkenyl succinic anhydride
- c) .001 - 10.0 percent by weight of a water soluble cationic vinyl addition polymer having a molecular weight greater than 10,000 and preferably less than 1,000,000.

11. The emulsion of claim 10 wherein the water soluble cationic vinyl addition polymer is selected from the group consisting of homo and copolymers of:

- a) diallyldimethyl ammonium chloride;
- b) methacrylamidopropyltrimethyl ammonium chloride;
- c) dimethylaminoethylmethacrylate;
- d) dimethylaminoethylmethacrylate quaternaries;
- e) dimethylaminoethylacrylate;
- f) dimethylaminoethylacrylate quaternaries;
- g) diethylaminoethylacrylate;
- h) diethylaminoethylacrylate quaternaries;
- i) acrylamide reacted with formaldehyde and a lower secondary amine through the Mannich reaction; and
- j) manniched acrylamide quaternaries.

12. In a method for the preparation of an emulsified alkenyl succinic anhydride sizing agent useful in the preparation of sized paper products, such emulsion containing water, an alkenyl succinic anhydride, and a cationic agent, the improvement comprising using as the cationic agent a water soluble cationic condensation polymer having an intrinsic viscosity of at least 0.15.
13. The method of claim 12 wherein the cationic condensation polymer is a polymer of epi-chlorohydrin and dimethylamine.
14. The method according to one of claims 12 or 13 wherein the polymer is added to the alkenyl succinic anhydride size emulsion so as to provide 0.01 - 10.0 parts by weight polymer for each part of alkenyl succinic anhydride contained in such emulsion.
15. The method according to one of claims 12 to 14 wherein the polymer is added to the alkenyl succinic anhydride size emulsion so as to provide from .05 - .9 parts by weight polymer for each part of alkenyl succinic anhydride present in such emulsion.
16. In a method for the sizing of paper using an alkenyl succinic anhydride size wherein an emulsion of alkenyl succinic anhydride is applied to the paper stock, the improvement comprising using as the emulsifier for the alkenyl

succinic anhydride size, a water soluble cationic condensation polymer having an intrinsic viscosity greater than 0.15.

17. The method of claim 16 wherein the cationic water soluble condensation polymer is a condensation polymer of epi-chlorohydrin and dimethylamine.

18. The method of claims 16 or 17 wherein the emulsion containing the water soluble polymer is added to the paper stock.

19. An emulsion of alkenyl succinic anhydride comprising:

- a) 50 - 99.0 percent by weight water
- b) 0.01 - 50 percent by weight of an alkenyl succinic anhydride
- c) .001 - 5.0 percent by weight of a water soluble cationic condensation polymer having an intrinsic viscosity greater than 0.15.

20. The emulsion of Claim 19 wherein the polymer is a condensation polymer of epi-chlorohydrin and dimethylamine.

Dr.Ro/oe

